INTRODUCTION

Chemical vapor deposition on the inside surface of a silica glass substrate tube (MCVD process) is among the most widely used vapor-phase processes for the fabrication of single-mode silica-based optical fiber preforms. Typically, the process utilizes high-temperature reactions of silicon tetrachloride and dopant halide (most frequently, GeCl\(_4\)) vapors with oxygen. A gas mixture is passed through a rotating silica glass tube, and an oxygen–hydrogen flame slowly traveling along the tube (usually, in the gas flow direction) initiates the reactions

\[
\text{SiCl}_4 + \text{O}_2 \rightarrow \text{SiO}_2 + 2\text{Cl}_2, \quad (1)
\]

\[
\text{GeCl}_4 + \text{O}_2 \leftrightarrow \text{GeO}_2 + 2\text{Cl}_2. \quad (2)
\]

The resulting oxide particles are deposited on the inside tube surface under the action of thermophoretic forces and are fused by the flame to form a transparent glass layer.

The effectiveness of the reactions in the gas flow can be characterized by the reaction time \(\tau\) and conversion \(\beta\). The latter is the ratio of the number of moles of a component in the reaction product to the initial number of moles of that component:

\[
\beta = \frac{N_1 - N_2}{N_1}, \quad (3)
\]

where \(N_1\) and \(N_2\) are the numbers of moles of the starting substance at the inlet and outlet of the reaction zone, respectively.

At typical MCVD temperatures, full SiCl\(_4\) conversion to silica takes on the order of 0.01 s \([1]\), whereas the GeCl\(_4\) conversion is 0.31 at this reaction time \([1]\) and takes 0.5 s to reach unity \([2]\).

At the same time, when reactions (1) and (2) are run concurrently, as is typical in the MCVD process, the GeO\(_2\) yield is ~0.5 even at reaction times close to 1 s \([3]\), which seems to be associated with the small equilibrium constant of reaction (2) \([1, 3]\). The considerable volume of additional molecular chlorine resulting from reaction (1) must reduce the GeO\(_2\) yield, especially because, in the MCVD process, the silicon tetrachloride concentration in the gas mixture, as a rule, notably exceeds the germanium tetrachloride concentration.

High-purity germanium tetrachloride is among the most expensive starting chemicals in the MCVD process. Clearly, a detailed understanding of the processes underlying the deposition of fiber preform material is of practical interest for the fabrication of both conventional germanium-doped silica glass fiber preforms and germania-glass-core preforms.

The purpose of this work was to study the effect of reaction time on the germania yield in the reaction of germanium tetrachloride with oxygen under typical MCVD fiber preform fabrication conditions.

EXPERIMENTAL AND RESULTS

Optimization of the reaction temperature. Our experiments were conducted in a standard MCVD apparatus for fiber preform fabrication, equipped with a system for forced cooling of the tube in the thermophoretic deposition zone \([4]\).

First, we optimized the GeCl\(_4\) conversion temperature. To this end, a gas mixture (table) was passed through the hot zone produced inside the tube by a torch (the maximum temperature of the outer tube surface was measured by an IR pyrometer with an accuracy of \(\pm 15^\circ\text{C}\)).
In our experiments, germanium tetrachloride was oxidized at different temperatures of the outer tube surface in the reaction zone, both individually (Fig. 1, curve 1) and in the presence of silicon tetrachloride (curve 2) or carbon tetrachloride (curve 3). The germanium tetrachloride concentration in the gas mixture at the tube outlet end was determined by IR spectroscopy.

In all of the experiments, the germanium tetrachloride conversion increased with increasing temperature in the reaction zone. The highest conversion was achieved when the temperature of the outer tube surface in the reaction zone was ~2000–2050°C. At this temperature, the GeCl$_4$ conversion in reaction (2) attained 80% (Fig. 1, curve 1). If reactions (1) and (2) were run concurrently, the GeCl$_4$ conversion was 60% (curve 2). The use of carbon tetrachloride instead of silicon tetrachloride reduced the GeCl$_4$ conversion to ~30% (the initial carbon tetrachloride concentration in the gas mixture was lower than the SiCl$_4$ concentration by more than a factor of 2).

It follows from the kinetic curves of reactions (1) and (2) [5] that the temperature range of reaction (1) is ~100°C wider than that of reaction (2). The temperature profile created by the traveling torch in the reaction zone (Fig. 2) is asymmetric along the tube axis, with a flat trailing edge and steep leading edge. Therefore, for a laminar gas-mixture flow and at moderate temperatures, the extent of reaction (2) in each section of a significant part of the reaction zone is a factor of 3–5 greater than that of reaction (1). For this reason, the excess chlorine concentration in the gas mixture in each section of the reaction zone must be substantially lower than might be expected. Replacing SiCl$_4$ with CCl$_4$, which reacts with oxygen at a considerably lower temperature in comparison with germanium tetrachloride, must raise the excess chlorine concentration in each section of the reaction zone compared to SiCl$_4$, which seems to be responsible for the lower germanium tetrachloride conversion.

If the above reasoning is correct, increasing the reaction time for concurrent reactions (1) and (2) must reduce germanium tetrachloride conversion.

**Effect of reaction time on GeCl$_4$ conversion.** The average reaction time in a flowing gas mixture can be determined as

$$
\tau = \frac{SI}{W},
$$

where $S$ is the cross-sectional area of the channel, $W$ is the volumetric flow rate of the gas mixture, and $l$ is the effective length of the reaction zone (hot zone). However, since only the temperature of the outer tube surface in the reaction zone was measured in our experiments, the true size of the hot zone inside the tube was difficult to determine. In connection with this, as a reaction time criterion we used the flow speed along the tube, $W/S$.

To assess the efficiency of germanium tetrachloride conversion in reaction (2) as a function of reaction time, a layer of SiO$_2$ particles was deposited on the inside tube surface by translating the flame in the direction opposite to the flow of a mixture of oxygen and silicon tetrachloride (SiCl$_4$ flow rate, 100 cm$^3$/min) (Fig. 3a).

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**Fig. 1.** Germanium tetrachloride conversion as a function of the outer-surface temperature in the reaction zone for different gas mixtures: (1–3) see the table.

**Fig. 2.** Axial temperature profile produced by the traveling torch.